

## SILICON SINGLE CRYSTAL AND ITS PRODUCTION

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### Abstract

**PROBLEM TO BE SOLVED:** To provide a method for producing a high-quality silicon single crystal with excellent device characteristics through Czochralski process.

**SOLUTION:** In this method for producing a silicon single crystal through crystal growth by Czochralski process, the crystal growth is performed in such an inert gas atmosphere so as to incorporate the grown crystal with hydrogen at a concentration of  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup> in the crystal and the ratio: V/G is set at such a critical value or lower that ring-shaped oxidation-induced laminating defects vanish at the crystal center (where, V is single crystal growth velocity, and G is the intracrystal temperature gradient in the growth direction within the temperature range from the melting point of silicon to 1,300 deg.C during single crystal growth process).

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**(57)[SUMMARY]**

**[OBJECT]**

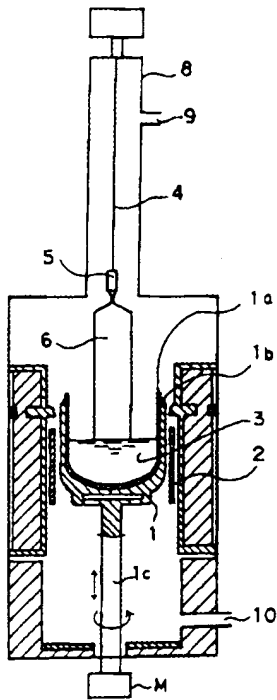
Offer a device characteristic with the manufacturing method of a superior high-performance silicon single crystal by the Czochralski method.

**[SUMMARY OF THE INVENTION]**

$^{1115}\text{atoms/cm}^3$

In the manufacturing method of the silicon single crystal which does crystal growth by the Czochralski method, while performing growth of a crystal in the inert-gas atmosphere where hydrogen of the concentration used as  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup> was added, in the grown-

up crystal, it is the silicon single crystal and the manufacturing method thereof which were grown in the ratios  $V/G$  with gradient  $G$  from growth-rate  $V$  of a single crystal, and the silicon melting point at the time of the single-crystal growth in the conditions set less than to the critical value to which a ring-like oxidation induction stacking fault disappears by the crystal centre the crystal inside-temperature degree of the growth direction in the temperature range to 1300 degrees C.



# [CLAIMS]

## [CLAIM 1]

A manufacturing method of a silicon single

crystal, in which in the manufacturing method of the silicon single crystal which does crystal growth by the Czochralski method, growth of a crystal is performed in the inert-gas atmosphere containing hydrogen.

Also, a ring-like oxidation induction stacking fault sets the ratios  $V/G$  with gradient  $G$  from growth-rate  $V$  of a single crystal, and the silicon melting point at the time of the single-crystal growth less than to the critical value which disappears by the crystal centre, the crystal inside-temperature degree of the growth direction in the temperature range to 1300 degrees C.

$^{1115}\text{atoms/cm}^3$

**[CLAIM 2]**

A manufacturing method of the silicon single crystal of above-mentioned Claim 1, in which in the manufacturing method of the silicon single crystal performed on above-mentioned conditions, hydrogen is added in an inert gas so that it may become the concentration whose hydrogen concentration of a growth in crystal is  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>.

**[CLAIM 3]**

A silicon single crystal, which is the silicon single crystal by which a crystal is grown by the Czochralski method.

Growth of a crystal is performed in the inert-gas atmosphere containing hydrogen. Also, the ratios  $V/G$  with gradient  $G$  are grown on the setting conditions less than the critical value to which a ring-like oxidation induction stacking fault disappears by the crystal centre, the crystal inside-temperature degree of the growth

direction in the temperature range from growth-rate V of a single crystal, and the silicon melting point at the time of the single-crystal growth to 1300 degrees C.

**[CLAIM 4]**

$^{1115}\text{atoms/cm}^3$

A silicon single crystal of above-mentioned Claim 3, in which in the silicon single crystal grown on above-mentioned setting conditions, a hydrogen concentration in crystal is grown on the conditions by which hydrogen of the concentration used as  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup> was added.

**[DETAILED DESCRIPTION OF INVENTION]****[0001]****[TECHNICAL FIELD]**

This invention becomes as follows about the manufacturing method of the silicon single crystal which is used as a semiconductor device.

In detail, it is related with the manufacturing method of the silicon single crystal grown by the Czochralski method (henceforth a CZ process).

**[0002]****[PRIOR ART]**

CzochralskiFloating Zone

There are various methods in manufacture of the silicon single crystal employed for a

semiconductor material.

However, CZ (Czochralski) method or FZ (Floating Zone) method is employed generally.

**[0003]**

A CZ process dips a seed crystal in this melt solution, after doing at a heater the heat fusion of the silicon polycrystal filled up into the quartz crucible.

It is the method of growing up a single crystal, by pulling up, whilst making this rotate.

**[0004]**

Moreover, FZ method does the heat fusion of part polycrystalline silicon ingot at high frequencies, and makes a fusion band.

It is the method of growing up a single crystal, making this fusion band move.

**[0005]**

Since the formation of the crystal of a large diameter is simple for the above-mentioned CZ process, the wafer cut down from the silicon single crystal manufactured by the CZ process is employed as a high degree-of-integration semiconductor-device substrate.

**[0006]**

(Oxidation induced Stacking  
Fault)Grown-in

In the crystal grown by the CZ process, a ring-like acid induction stacking fault (henceforth OSF (Oxidation induced Stacking Fault)) may occur according to crystal-growth conditions.

In addition, some kinds of micro defects (henceforth a Grown-in defect) are formed.

**[0007]**



The generating region in the crystal of OSF ring is determined by the ratios  $V/G$  of temperature-gradient  $G$  in the crystal of growth-rate  $V$  of a single crystal, and the silicon melting-point - 1300 degree C raising axial direction of the single crystal grown.

**[0008]**

When OSF ring has ratios  $V/G$  larger than the critical value (it merely describes as a critical value hereafter) which disappears by the in-crystal centre part, a porosity condenses and the cavernous (void) defect which made the about 0.1-micrometer octahedron the basic structure is formed.

**[0009]**

Meanwhile, when ratios  $V/G$  are smaller than a critical value, the silicon between lattices condenses and the transition cluster is formed.

**[0010]**

The wafer generally employed as a semiconductor-device substrate is a wafer cut down from the single crystal grown up on the conditions on which a void is formed.

This void makes the oxide-film breakdown voltage which is one of the electrical properties of a semiconductor device reduce.

**[0011]**

In the crystal, in order to make the number of voids per unit volume (defective density) reduce, the method slow-cooled in the temperature area (about 1100 degrees C ) in which a void is formed at the time of crystal

growth is performed.

[0012]

**[PROBLEM ADDRESSED]**

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However, by this method, even when a defective density can reduce only to about  $10^5\text{cm}^{-3}$  and a defective density is reduced, it is revealed that size of a defect makes it big and rough.

The further improvement is required in the silicon growing of a single crystal employed for the semiconductor device of a next generation.

[0013]

Here, as for the wafer cut down from the single crystal grown on the conditions which ratios  $V/G$  become less than a critical value, a void does not exist. Therefore, an oxide-film breakdown voltage characteristic becomes excellent.

However, since the transition cluster exists, an above-mentioned wafer degrades a pn-junction leak characteristic.

[0014]

Grown-in

Then, this invention aims at offering high-performance-isation of a silicon single crystal, and the manufacturing method of the possible silicon single crystal of obtaining a high-performance single crystal excluding a void and Grown-in defects, such as the transition cluster.

[0015]

**[SOLUTION OF THE INVENTION]**

In the manufacturing method of the silicon single crystal which does crystal growth of the invention described to this-application 1st Claim by the Czochralski method, growth of a crystal is performed in the inert-gas atmosphere containing hydrogen. It is the manufacturing method of the silicon single crystal of composition of setting the ratios  $V/G$  with gradient  $G$  from growth-rate  $V$  of a single crystal and the silicon melting point at the time of the single-crystal growth also less than to the critical value to which a ring-like oxidation induction stacking fault disappears by the crystal centre, the crystal inside-temperature degree of the growth direction in the temperature range to 1300 degrees C.

**[0016]**

A void will not be generated if a crystal is grown up on the conditions which make ratios  $V/G$  less than a critical value as mentioned above.

Moreover, if a crystal is grown in the inert-gas atmosphere containing hydrogen gas, the transition cluster will not occur.

Hydrogen gas by which this is contained in inert-gas atmosphere melts into silicon melt solution.

When melt solution solidifies, hydrogen gas is received in a single crystal.

Or, after solidifying under high temperature, a single crystal receives directly.

And, since hydrogen gas received in the single crystal may suppress a diffusion of the silicon atom between lattices, aggregation of

the silicon atom between lattices does not occur and the transition cluster does not occur as a result.

[0017]

Grown-in

Thus, on the conditions set up so that it might become V/G value less than a critical value in the inert-gas atmosphere containing hydrogen gas, if crystal growth is performed, the high-performance growing of a single crystal on which Grown-in defects, such as a void and the transition cluster, are not formed will be made.

[0018]

$^{1115}$ atoms/cm<sup>3</sup>

In the manufacturing method of the silicon single crystal performed on condition of above-mentioned Claim 1, invention described to this-application 2nd Claim is the manufacturing method of the silicon single crystal of composition of that hydrogen is added in an inert gas so that it may become the concentration whose hydrogen during growth crystal is  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>.

[0019]

In the Czochralski method which performs crystal growth under reduced pressure, if hydrogen more than the 5% concentration is added in inert-gas atmosphere, a huge abnormal defect will be formed during a crystal. Moreover, a carbon heater reacts with hydrogen.

Reaction used as methane becomes intense.

The problem from which the impure element in methane or carbon is the pollution cause of a crystal is produced.

Moreover, there is a possibility that problems, that is, heater exhaustion and deterioration becomes intense, may be produced.

**[0020]** $^{11}\text{atoms/cm}^3$   $^{15}\text{atoms/cm}^3$ 

Moreover, the hydrogen concentration in a silicon single crystal of there being a transition cluster inhibitory effect is  $5 \times 10^{11}$  atoms/cm<sup>3</sup> or more.

The hydrogen concentration which produces the huge abnormal defect mentioned above is  $1 \times 10^{15}$  atoms/cm<sup>3</sup> or more.

**[0021]** $^{115}\text{atoms/cm}^3$  Grown-in

Therefore, in this invention, a hydrogen concentration in crystal is set as  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>.

The high-performance growing of a single crystal on which Grown-in defects, such as a void and the transition cluster, are not formed is enabled.

**[0022]**

Invention described to this-application 3rd Claim is a silicon single crystal by which a crystal is grown by the Czochralski method.

While growth of a crystal is performed in the inert-gas atmosphere containing hydrogen, the ratios V/G with gradient G are the silicon single crystals of composition of being grown on the setting conditions less than the critical value to which a ring-like oxidation induction stacking fault disappears by the crystal centre the crystal inside-temperature degree of the growth direction in the temperature range from growth-rate V of a single crystal, and the silicon melting

point at the time of the single-crystal growth to 1300 degrees C.

**[0023]**

$^{1115}\text{atoms/cm}^3$

The silicon single crystal by which invention described to this-application 4th Claim is grown on above-mentioned setting conditions in invention of above-mentioned Claim 3 is a silicon single crystal of composition of that a hydrogen concentration in crystal is grown on the conditions by which hydrogen of the concentration used as  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup> was added.

**[0024]**

In the inert-gas atmosphere containing such hydrogen gas, if ratios V/G grow up a single crystal on the conditions which become less than a critical value, the high-performance silicon single crystal without defects, such as a void and the transition cluster, can be obtained.

**[0025]**

$^{1115}\text{atoms/cm}^3$

Moreover, a high-performance silicon single crystal can be obtained by growing up a silicon single crystal on the conditions set up so that a hydrogen concentration in crystal might become  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>.

**[0026]**

**[Embodiment]**

Hereafter, this invention is explained in detail.

**[0027]**

Figure 1 is a schematic block diagram of the single-crystal growth apparatus using the CZ process employed for the manufacturing method of this invention.

**[0028]**

As shown in Figure 1, 1 shows a quartz crucible.

This crucible 1 consists of the inside-layer hold container 1a made from quartz of a bottomed cylindrical shape, and the same outer-layer hold container 1b made from the graphite of a bottomed cylindrical shape by which the fitting was done to the outer side of this inside-layer hold container 1a.

**[0029]**

The crucible 1 which consists of such composition is supported by support shaft 1c rotated at a predetermined speed.

The heater 2 is arranged by the outer side of a crucible 1 at the concentric cylindrical shape.

The melt 3 of the raw material by which the fusion was done as for heat of the above-mentioned heater 2 is filled up into the interior of this crucible 1.

It pulls up to the centre of a crucible 1, and the raising shafts 4, such as a stick or a wire, are arranged.

The point of this raising shaft 4 is made to contact a seed chuck and the seed crystal 5 on the surface of a melt 3.

**[0030]**

Furthermore, making the raising shaft 4 rotate in the crucible 1 and the opposite direction

which are rotated by support shaft 1c, at a predetermined speed, by pulling up a seed crystal 5, the coagulate of the melt 3 is done at the end of a seed crystal 5, and a single crystal 6 is grown up.

In addition, 9 and 10 are the feed hoppers and the drain holes of a controlled atmosphere in the drawing(s).

**[0031]**

In order to do the non-dislocation of the crystal initially at the time of a growing of a single crystal, a seed iris diaphragm is performed.

**[0032]**

Then, a shoulder is formed in order to secure the body diameter of a single crystal.

The thing of the shoulder changed is performed in the place which became the body diameter.

A body diameter is fixed and it transfers to growth of a single-crystal main body.

If the single crystal of predetermined length is grown for a body diameter, the tail aperture for detaching a single crystal from a melt in the state of non-transition will be performed.

**[0033]**

Growth-rate  $V$  of a single crystal is drawing-of-a-single-crystal speed.

Moreover, growth-rate  $V$  can be changed, uniformly maintained the diameter of a single crystal by changing the temperature of a melt 3.

**[0034]**

Moreover, temperature-gradient  $G$  measures crystal temperature in 1400 degrees C near the



silicon melting point on an identical shaft generally parallel to the raising direction, and 1300 degrees C.

It computes as temperature-gradient  $G$  which is the ratio of the temperature gradient of that value, and the interval for 2 points.

**[0035]**

This temperature-gradient  $G$  can be changed by altering the thermal environment of a furnace interior.

**[0036]**

Next, the crystal-growth apparatus shown in Figure 1 is employed.

The Example which performed the silicon growing of a single crystal is shown.

**[0037]**

(Example 1) In this example,  $V/G$  value becomes less than a critical value by making rate-of-crystal-growth  $V$  less than into 0.4 mm/min.

**[0038]**

A single crystal is grown by above-mentioned rate-of-crystal-growth  $V$  (0.4 mm/min), without adding hydrogen.

After performing a predetermined sample process, the defective density in a crystal was measured by the seco etching.

**[0039]**

The transition cluster about  $10^4\text{cm}^{-3}$  was detected by the grown crystal in hydrogen unadded conditions.

**[0040]**

Moreover, it is rate-of-crystal-growth  $V$  0.4 mm/min. A crystal is grown in the conditions (40 litres/min. of an argon rate of flow, and 0.4 litres/min.) of a hydrogen rate of flow.

After performing a predetermined sample process, the defective density in a crystal was measured by seco etching.

**[0041]**

The transition cluster was not detected by the crystal grown in above-mentioned hydrogen-addition conditions.

The hydrogen concentration in crystal grown in this hydrogen condition was  $5 \times 10^{11} \text{cm}^{-3}$ .

**[0042]**

Thus hydrogen is added in an inert gas so that a hydrogen concentration in crystal may be predetermined value.

If  $V/G$  value performs crystal growth on the conditions which become less than a critical value, the high-performance silicon single crystal by which the grown-up crystal does not have generating of a void since  $V/G$  value is less than critical values, and generating of the transition cluster is not confirmed, either can be obtained.

**[0043]**

Next, above-mentioned Example 1 and above-mentioned identical apparatus are employed.

Moreover, Example 1 and the Example at the time of performing crystal growth in the conditions which have an identical temperature-

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gradient G value are shown.

**[0044]**

(Example 2) In this example, V/G value makes more than a critical value by making rate-of-crystal-growth V into 1.0 mm/ min.

**[0045]**

A single crystal is grown by above-mentioned rate-of-crystal-growth V (0.4 mm/ min), without adding hydrogen.

After performing a predetermined sample process, the defective density in a crystal was measured by seco etching.

**[0046]**

The void about 106 cm-3 was detected by the grown crystal in hydrogen unadded conditions.

**[0047]**

Moreover, it is above-mentioned rate-of-crystal-growth V 1.0 mm/ min. A crystal is grown in the conditions (40 litres/min. of an argon rate of flow, and 0.4 litres/min.) of a hydrogen rate of flow.

After performing a predetermined sample process, the defective density in a crystal was measured by seco etching.

**[0048]**

The void about 106 cm-3 was detected like the crystal grown on hydrogen unadded conditions by the crystal grown in above-mentioned hydrogen-addition conditions.

**[0049]**

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6-3

When growth-rate V was set up and the crystal growth was performed by this example so that it might become V/G value more than a critical value, hydrogen unadded conditions are attained and generating of a void was similarly confirmed in hydrogen-addition conditions.

#### [0050]

$^{1115}\text{atoms/cm}^3$

Thus, V/G value is set less than to a critical value.

If crystal growth is performed on the conditions which added hydrogen gas in the inert gas so that a hydrogen concentration in crystal may become  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>, the high-performance silicon single crystal which does not have a void and the transition cluster during the grown-up crystal can be obtained.

#### [0051]

#### [EFFECT OF THE INVENTION]

$^{1115}\text{atoms/cm}^3$

As explained above, in the manufacturing method of the silicon single crystal which does crystal growth of this invention by the Czochralski method, growth of a crystal is performed in the inert-gas atmosphere containing hydrogen. Also, a ring-like oxidation induction stacking fault sets the ratios V/G with gradient G less than to the critical value which disappears by the crystal centre, the crystal inside-temperature degree of the growth direction in the temperature range from growth-rate V of a single crystal, and the silicon melting point at the time of the single-crystal growth to

1300 degrees C.

A hydrogen concentration in crystal is the manufacturing method of the silicon single crystal manufactured in the silicon single crystal grown by adding hydrogen in inert-gas atmosphere so that it may become  $5 \times 10^{11}$  to  $1 \times 10^{15}$  atoms/cm<sup>3</sup>, and above-mentioned conditions.

**[0052]**

Thus, by making V/G value less than into a critical value, while doing generating control, it receives during the crystal as which hydrogen which is a void, and which was added in inert-gas atmosphere was grown.

A diffusion of the silicon atom between lattices is suppressed.

Generating of the transition cluster can be eliminated, without aggregation of the silicon atom between lattices occurring.

**[0053]**

Therefore, according to the method of this invention, the defect-free crystal without generating of a void and the transition cluster is raisable.

High-performance-isation of a silicon single crystal can be attained.

**[BRIEF EXPLANATION OF DRAWINGS]**

**[FIGURE 1]**

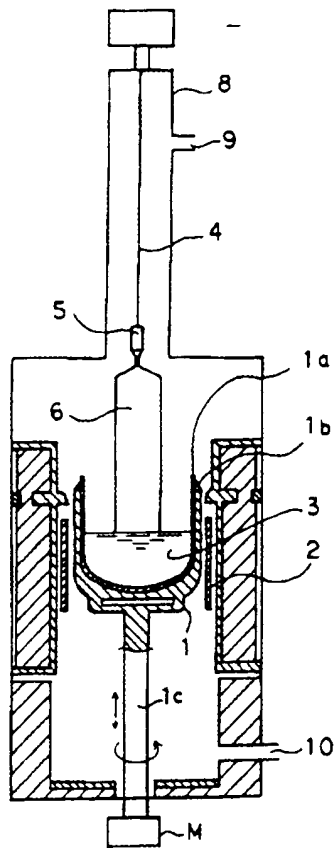
It is the schematic block diagram of the single-crystal-growth apparatus which concerns on this invention and is employed for the growing

of a single crystal by the CZ process.

**[EXPLANATION OF DRAWING]**

- 1 Crucible
- 1a Inside-layer hold container
- 1b Outer-layer hold container
- 1c Support shaft
- 2 Heater
- 3 Melt
- 4 Raising Shaft
- 5 Seed Crystal
- 6 Single Crystal
- 9 Feed Hopper of Controlled Atmosphere
- 10 Drain Hole of Controlled Atmosphere
- M Motor

**[FIGURE 1]**



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